



Efficient degradation of refractory organics for carbonate-containing wastewater via generation carbonate radical based on a photoelectrocatalytic TNA-MCF system

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ABSTRACT

Carbonate widely exist in wastewater and natural water. Here we proposed an efficient refractory organics degradation method for carbonate-containing wastewater via generating carbonate radical based on a photoelectrocatalytic TNA-MCF system. In the system, TiO₂ nanotube arrays (TNA) and modified carbon felt (MCF) were used as photoanode and cathode, respectively. HCO₃[−] was used as electrolyte. The results show that the system achieved 85.78% removal rate after 120 min in rhodamine B degradation, which is 30% higher than that using SO₄^{2−} as electrolyte. The excellent performance is attributed to the strong oxidation of [•]CO₃[−] to organics, which originates from the reactions between HCO₃[−] and h_ν⁺ on TNA photoanode. It was also generated from the activation of HCO₃[−] with H₂O₂ or O₂^{•−} on MCF cathode. Moreover, the mechanism of [•]CO₃[−] formation and its efficient degradation of organics were investigated. These results demonstrate that this system has a potential application in refractory organics degradation.

1. Introduction

With the rapid development of industries, the pollution generated from wastewater containing refractory organic contaminants is becoming more and more serious, which severely threatens human's health and social development [1,2]. However, traditional treatment methods like physicochemical and biochemical processes have one or more drawbacks like low efficiency and creating secondary pollutants [3], which is hard to meet the standards of degradation.

To solve these problems, the advanced oxidation technology including photoelectrocatalysis (PEC) technology, a kind of photocatalytic (PC) technology assisted by electrochemistry, has gotten broad development through the formulation of hydroxyl radical to enhance the degradation of organic matters [4–6]. Compared with traditional PC method, PEC method would facilitate the separation of photogenerated electron/hole pairs and thus strengthen the mineralization of organic

pollutants [7–11]. It is generally believed that bi/carbonate in water can inhibit the oxidative activity of hydroxyl radical because of its capture effect. Therefore, there are rare studies about carbonate-containing wastewater in the advanced oxidation system.

Compared with [•]OH radical (E₀ = 2.3 V, pH 7), although [•]CO₃[−] radical is relatively less reactive (E₀ = 1.78 V, pH 7) [12], it still has a series of merits for its application in wastewater treatment. For instance, (1) as a strong one-electron oxidant, [•]CO₃[−] reacts more fast and selectively with electron-rich moieties like aromatic anilines, nitrogen containing compounds and sulfur containing compounds via electron transfer and hydrogen abstraction [13]. (2) [•]CO₃[−] radical has longer lifetime than [•]OH and the radical-radical recombination of [•]CO₃[−] (k = 2 × 10⁷ M^{−1}s^{−1}) is much lower than the reaction of [•]OH (k = 5.5 × 10⁹ M^{−1}s^{−1}) with itself [14]. (3) the steady-state concentration of [•]CO₃[−] (10^{−13} ~ 10^{−15} M) in natural aqueous environment is two orders of magnitude higher than that of [•]OH (10^{−14} ~ 10^{−18} M) [15–17],

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which make it possible to react with contaminants more adequately [18]. In addition, HCO_3^- can activate H_2O_2 to generate many free radicals like $\text{O}_2^{\cdot-}$ and $\cdot\text{CO}_3^-$ to oxidize refractory pollutants. [19–21]. On top of that, the existing $\text{O}_2^{\cdot-}$ will also facilitate the production of $\cdot\text{CO}_3^-$ in HCO_3^- solution [22]. These evidences indicate that $\cdot\text{CO}_3^-$ could have affluent sources. Based on overall consideration, $\cdot\text{CO}_3^-$ radical could unexpectedly promote organic pollutants degradation in some cases. Unfortunately, few people have studied its application in PEC systems.

Hence, we proposed an efficient refractory organics degradation method in carbonate-containing wastewater via generating carbonate radical based on a photoelectrocatalytic TNA-MCF system. In the system, TiO_2 nanotube arrays (TNA) and modified carbon felt (MCF) were used separately as photoanode to generate the valence hole (h_{vb}^+) and cathode to produce H_2O_2 . The low-cost and low-polluting HCO_3^- anion was used as electrolyte to produce $\cdot\text{CO}_3^-$.

Results show that when using RhB as model refractory organics, the degradation efficiency of the novel system is even apparently higher than that of traditional sulfate electrolyte system. The effects of initial pH and HCO_3^- concentration were also investigated. The mechanism of $\cdot\text{CO}_3^-$ formation and its efficient degradation of other typical organic compounds have been studied. This work indicates a possibility to develop an economical and efficient $\cdot\text{CO}_3^-$ radical based PEC system for refractory pollutants treatment.

2. Experimental

2.1. Materials

The carbon felt (thick 3 mm) was purchased from Beijing Jinglong Carbon Material Co., Ltd. Titanium sheet was purchased from KurumiWorks (Japan). Methylene blue (MB), methyl orange (MO), rhodamine B (RhB), congo red (CA), p-nitrophenol (PNP), tetracycline (TE), sodium bicarbonate, sodium sulfate, hydrofluoric acid, potassium iodide, isopropanol and tertiary butanol were all purchased from Sinopharm chemical reagent Co., LTD. Unless otherwise indicated, all chemicals used in this experiment were of analytical reagent grade. All the solutions were prepared by deionized (DI) water from a Milli-Q ultrapure water system.

2.2. Preparation of TNA photoanode

According to the method mentioned by previous articles [23], titanium sheets, cut into several pieces ($2\text{ cm} \times 5\text{ cm}$), were cleaned by the mixture of HF, HNO_3 and DI water (1 : 4 : 5) and then dried by a heated blower. Electrochemical anodization was performed by using a DC power supply (TRADEX MPS 305, 0–60 V, 0–5 A). The anodization process was performed under indoor temperature in 0.5 wt % HF solution with Pt sheet ($2 \times 2\text{ cm}$) as a counter electrode for 30 min. After that, the TNAs were acquired by annealing at 450°C for 3 h in the air with heating and cooling rate of $1^\circ\text{C}/\text{min}$.

2.3. Preparation of MCF cathode

The modified carbon felt (MCF) was prepared by using anodic polarization method [24]. The blank carbon felt (CF) sheet was firstly cut into samples of $2\text{ cm} \times 5\text{ cm}$, then ultrasonically washed by acetone, ethanol and DI water for 30 min, respectively. Pt sheet ($1 \times 1\text{ cm}$) was offered as the counter electrode and saturated calomel electrode (SCE) was employed as the reference electrode. The cyclic polarization process was carried out in 10 wt % H_2SO_4 solution with the range from 0.0 V to +2.0 V at a speed of 0.01 V/s for 14 segments. Thereafter, MCF electrode was obtained by vacuum drying at 50°C for 10 h.

2.4. Characterization of the electrode

The morphologies of the electrodes were represented by a Field Emission Scanning Electron Microscopy instrument (FE-SEM; Zeiss, Germany, ULTRA PLUS). Specially, Fourier transformation infrared spectrum (FT-IR) was recorded by a Nicolet6700 instrument. X-ray photoelectron spectra (XPS) was investigated by an AXIS Ultra DLD instrument (Kratos, Shimadzu) with nonchromatic Al K α radiation at 12 kV and X-ray diffraction (XRD, Rigaku D-Max B) was used to characterize crystal form of the electrode.

2.5. Degradation experiments

The degradation experiments were processed in a quartz reactor ($25\text{ mm} \times 40\text{ mm} \times 50\text{ mm}$) under simulate UV light by Xe lamp ($100\text{ mW}/\text{cm}^2$, Perfect Light, China). The initial voltage was 0.5 V and pH was 8.3. In the system, the TNA electrode, the MCF and SCE were employed as photoanode, cathode and reference electrode, respectively. Each experiment was conducted for two hours. In a typical degradation experiment, the concentrations of reactants in the system were: NaHCO_3 0.05 M, RhB 20 mg/L. During degradation process, about 3 mL sample was taken every half an hour to detect at its maximum absorption on a UV-VIS spectrophotometer (752N ZG001, INESA, Shanghai). Each time after detection, the 3 mL sample was quickly poured back into the reactor.

3. Results and discussion

3.1. Degradation of RhB in TNA-MCF system

To test the practicability of photoelectrocatalytic (PEC) TNA-MCF system using HCO_3^- anion as electrolyte (TNA-MCF/ HCO_3^-) for organic degradation, rhodamine B (RhB) was selected as the targeted pollutant. The PEC TNA-MCF system using SO_4^{2-} anion (TNA-MCF/ SO_4^{2-}), PEC TNA-Pt black system using HCO_3^- anion (TNA-Pt black/ HCO_3^-) and SO_4^{2-} anion (TNA-Pt black/ SO_4^{2-}) were performed respectively as comparison. Considering the buffering effect of HCO_3^- , all of the experiments were conducted at pH 8.3. The initial concentration of RhB was 20 mg/L. Fig. 1a shows the concentration change of RhB in different cathodes and electrolytes systems with 0.5 V initial voltage and 0.05 M electrolyte. It can be observed from Fig. 1a that there is little sign of degradation in these four PEC systems under dark condition. When exposed to light, the RhB removal ratio after 120 min could reach 35.18%, 46.47%, 55.37% and 85.78% in TNA-Pt black/ SO_4^{2-} , TNA-Pt black/ HCO_3^- , TNA-MCF/ SO_4^{2-} and TNA-MCF/ HCO_3^- system, respectively. The RhB degradation efficiency after 120 min in TNA-Pt black/ HCO_3^- system was 46.47%, which is slightly over 10% higher than that in TNA-Pt black/ SO_4^{2-} system. The result is probably attributed to the strong oxidation of carbonate ($\cdot\text{CO}_3^-$) radical to organics, which caused by the reactions between bicarbonate (HCO_3^-) and the valence hole (h_{vb}^+) on the surface of TNA photoanode [25]. When using MCF as cathode, the degradation rate of RhB would be greatly improved in both HCO_3^- and SO_4^{2-} solution. The generation of H_2O_2 and $\text{O}_2^{\cdot-}$ radical on the MCF cathode surface would promote the oxidation efficiency. In particular, 85.78% of RhB was removed after 120 min in TNA-MCF/ HCO_3^- system. In contrast, there was only 55.37% of RhB degradation in TNA-MCF/ SO_4^{2-} system under the same condition. This is maybe more $\text{O}_2^{\cdot-}$ and $\cdot\text{CO}_3^-$ radicals can be generated from the activation of H_2O_2 with HCO_3^- under this condition [26]. Besides, the existing $\text{O}_2^{\cdot-}$ would also react with HCO_3^- to strengthen $\text{CO}_3^{\cdot-}$ radical production and thus enhance the degradation efficiency [12,27]. The detailed mechanism can be seen in 3.3.

Generally speaking, HCO_3^- anion is often regarded as a kind of $\cdot\text{OH}$ radical scavenger. However, the generated $\cdot\text{CO}_3^-$ radical in the system even promote the degradation process. Although $\cdot\text{CO}_3^-$ radical is relatively less reactive than $\cdot\text{OH}$ radical, it still possesses some special

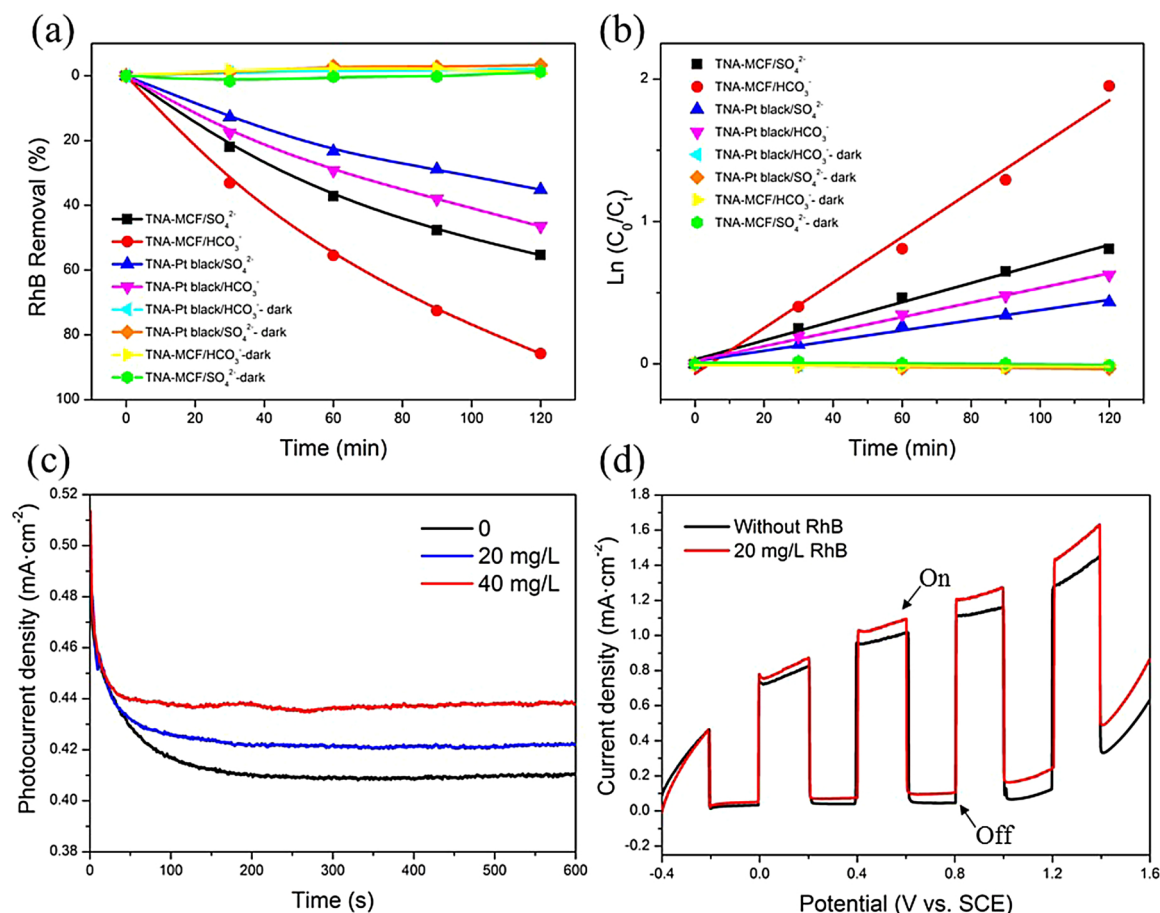


Fig. 1. (a) Time profiles of the RhB degradation in different systems. (b) Plots of $\ln(C_0/C_t)$ versus time for the RhB degradation in different systems. (c) I-t curve of TNA-MCF/ SO_4^{2-} system with different RhB concentration. (d) The chopped LSV with or without RhB in TNA-MCF/ HCO_3^- system at scan rate of 0.025 V/s.

features such as its high selectivity, low radical-radical recombination rate and long lifetime in water, which would be conducive to some organic pollutants degradation [28].

In order to further analyze the degradation effect of rhodamine B, the kinetic equation was introduced:

$$\ln\left(\frac{C_0}{C_t}\right) = kt$$

In this equation, k is the apparent reaction constant, C_0 is the initial concentration, and C_t is the concentration after t min. As shown in Fig. 1b, the degradation of rhodamine B obeys the quasi-first-order reaction kinetics. In the TNA-MCF/ HCO_3^- system, k could reach 0.01587 min^{-1} , which was 2.4 times that of TNA-MCF/ SO_4^{2-} system, and even 4.5 times that of TNA-Pt/ SO_4^{2-} system. Moreover, the photoelectrochemical behavior of TNA-MCF/ HCO_3^- system was investigated. The I-t curve of TNA-MCF/ HCO_3^- system with different RhB concentration is shown in Fig. 1c. The photocurrent is very stable and can get improved with the increase of RhB concentration. The chopped LSV with or without RhB in TNA-MCF/ HCO_3^- system is shown in Fig. 1d. The plots reveal that TNA has positive photocatalytic ability under light irradiation. The photocurrent in the system would grow higher with the addition of pollutant, which could facilitate charge separation and further contribute to the pollutant degradation. Above all, it can be concluded that TNA-MCF/ HCO_3^- system owns overall superiority in pollutant degradation.

3.2. Effects of different factors on the degradation of RhB

3.2.1. HCO_3^- concentration

In order to study the best HCO_3^- concentration in TNA-MCF/

HCO_3^- system, the effect of different HCO_3^- concentrations on the performance of the system was performed. The effect of different HCO_3^- concentrations ranging from 0 to 0.1 M on 20 mg/L RhB degradation is shown in Fig. 2a and b. When there is no bicarbonate anion in the solution under the same condition, only 31.51% RhB degraded in the system. When the concentration of bicarbonate anion added to 0.01 M, the degradation efficiency was 49.13% after 120 min reaction. With the increase of HCO_3^- , the degradation efficiency was considerably improved. For instance, the RhB removal rate were 85.78% in 0.05 M HCO_3^- . However, the degradation rate slightly decreased with higher concentration of HCO_3^- (0.1 M). This phenomenon indicated that 0.05 M HCO_3^- was saturated to the experiment.

3.2.2. pH value

Since the bicarbonate anionic forms were different in different pH conditions, we studied the effect of initial pH values on the degradation of RhB. As shown in Fig. 2c and d, RhB could be effectively degraded in the TNA-MCF/ HCO_3^- system when pH was approximately at 8.3. When pH decreased from 8.3 to 4.3, the degradation efficiency decreased from 82.13% to 66.48%, then slightly increased to 68.41%. Because as the decrease of pH, the portion of bicarbonate anion will be reduced and at the same time carbonic acid will get improved. Carbonic acid was very unstable and could be easily transformed to dissociative CO_2 . Similarly, with the increase of pH from 8.3 to 10.3, the degradation rate fell from 82.13% to 59.98% because of the conversion of bicarbonate into carbonate which would inhibit the generation of carbonate radical on electrode. Therefore, the optimal pH for degradation was 8.3.

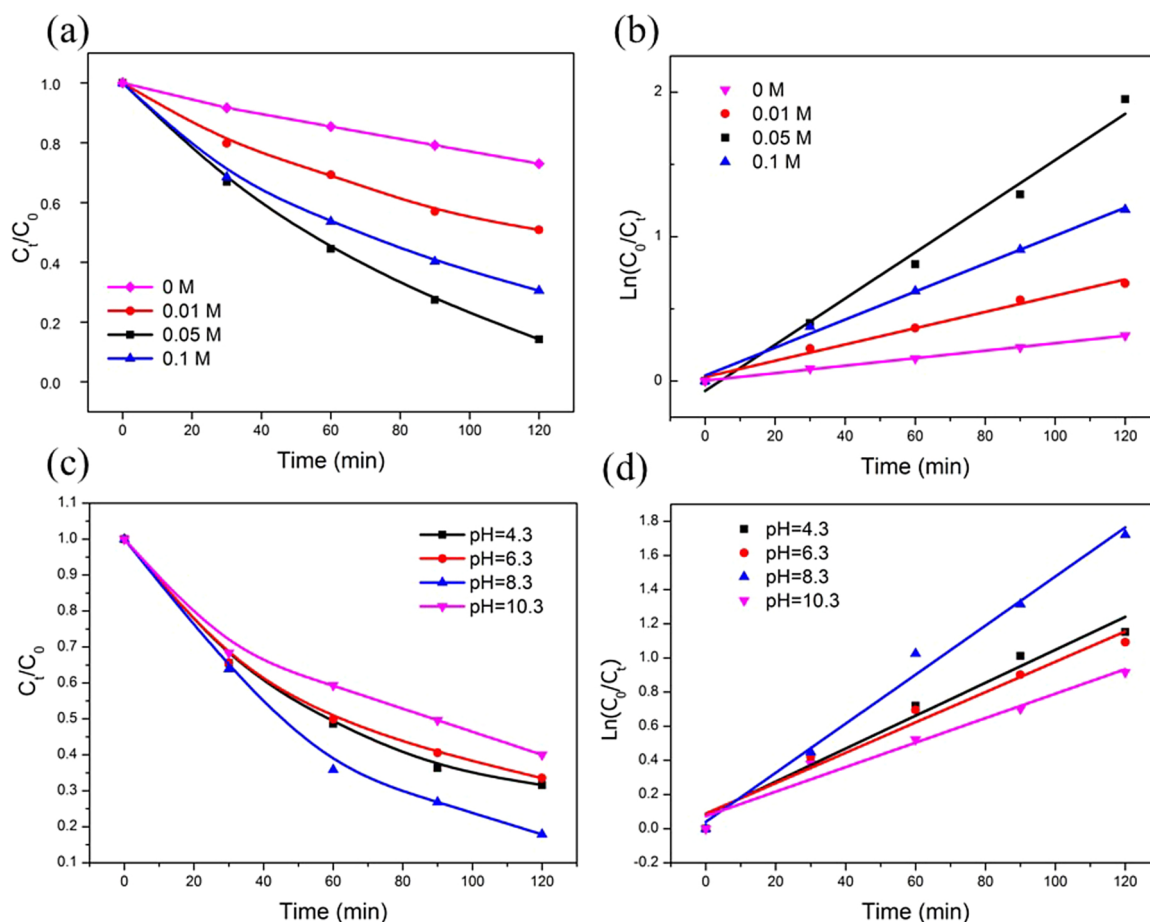


Fig. 2. Operation effects of TNA-MCF/ HCO_3^- system on RhB degradation: (a) and (b) HCO_3^- concentration; (c) and (d) pH value.

3.3. Mechanism of RhB degradation in TNA-MCF/ HCO_3^- system

Based on the above results and discussion, the operating mechanism based on $\cdot\text{CO}_3^-$ radical for highly efficient RhB degradation in TNA-MCF/ HCO_3^- system was proposed (Fig. 6). In the initial stage, under light illumination at TNA photoanode, the electrons and holes were generated at the valence band (VB) and conduction band (CB) separately [29,30]. The detailed characterization of TNA photoanode is provided in the supporting information. The photogenerated holes would oxidize HCO_3^- anion to generate $\text{CO}_3^{\cdot-}$ radical. The main equations can be represented as follows (Eqs (1)–(2)):



The photoexcited electrons would migrate to the cathode via an external voltage, which can react with O_2 to generate $\text{O}_2^{\cdot-}$ radical via the one-electron process and H_2O_2 via the two-electron process as follows (Eqs. (3)–(4)) [31]:



The generation of H_2O_2 relied on the characteristics of cathode used. The characterization of MCF were shown as follow. The original carbon felt was used as comparison.

Fig. 3 shows the characterization of carbon felt before and after modification by 10 wt % H_2SO_4 , including SEM, XPS, FT-IR and H_2O_2 production analysis. As can be seen from SEM images (Fig. 3a–d), the untreated carbon felt showed a smooth surface while the surface became much rougher after modification. The increased roughness would

be helpful to the increase of active $-\text{OH}$ group on the carbon fibers [32]. In C1s XPS spectra (Fig. 3e), the peak at 284.8 eV, 286.1–286.3 eV, 287.5 eV and 288.9 eV were attributed to C–C, C=O, C–OH and $-\text{COOH}$, respectively [33]. The relative functional groups contents based on calculated peak area were shown in Table S1. The content of C–OH after modification was slightly higher than that of original one. In O1s spectra (Fig. 3f), the peak at 531.5 eV, 533.5–534 eV and 532.2–533.4 eV were assigned to C=O, $-\text{COOH}$ and C–OH, respectively [32]. It can be seen that the contents of $-\text{COOH}$ and C–OH in modified CF was remarkably higher than those in original ones. As previous articles mentioned, the oxygen-containing groups would increase the ORR activity and facilitate the 2-electron-reduction path and thus enhance the H_2O_2 production [34,35]. In FT-IR spectrum (Fig. 3g), it can be found that there was hardly any distinct peak in original CF sample. While in modified sample, there were two peaks located at 1632 and 3281 cm^{-1} which were ascribed to carboxylic C=O and the stretching vibration of $-\text{OH}$, respectively [36]. This is consistent with XPS analysis. Furthermore, the concentration of H_2O_2 (Fig. 3h) was measured via the potassium titanium oxalate method [37]. It can be seen that the concentration of H_2O_2 obtained by modified-CF was continuously increased in 120 min and could reach its highest concentration of 0.4881 mmol/L, which is 3 times higher than that of blank-CF.

Then, the H_2O_2 generated at the MCF cathode would be activated by HCO_3^- anion to produce $\text{O}_2^{\cdot-}$ and $\cdot\text{CO}_3^-$ radicals [16,20,38]. Particularly, the abundant $\text{O}_2^{\cdot-}$ radical would also contribute to $\cdot\text{CO}_3^-$ generation in HCO_3^- solution [22,27,39]. The increasing number of radicals produced in the whole system would greatly enhance organic pollutants degradation (Eqs 5–6).

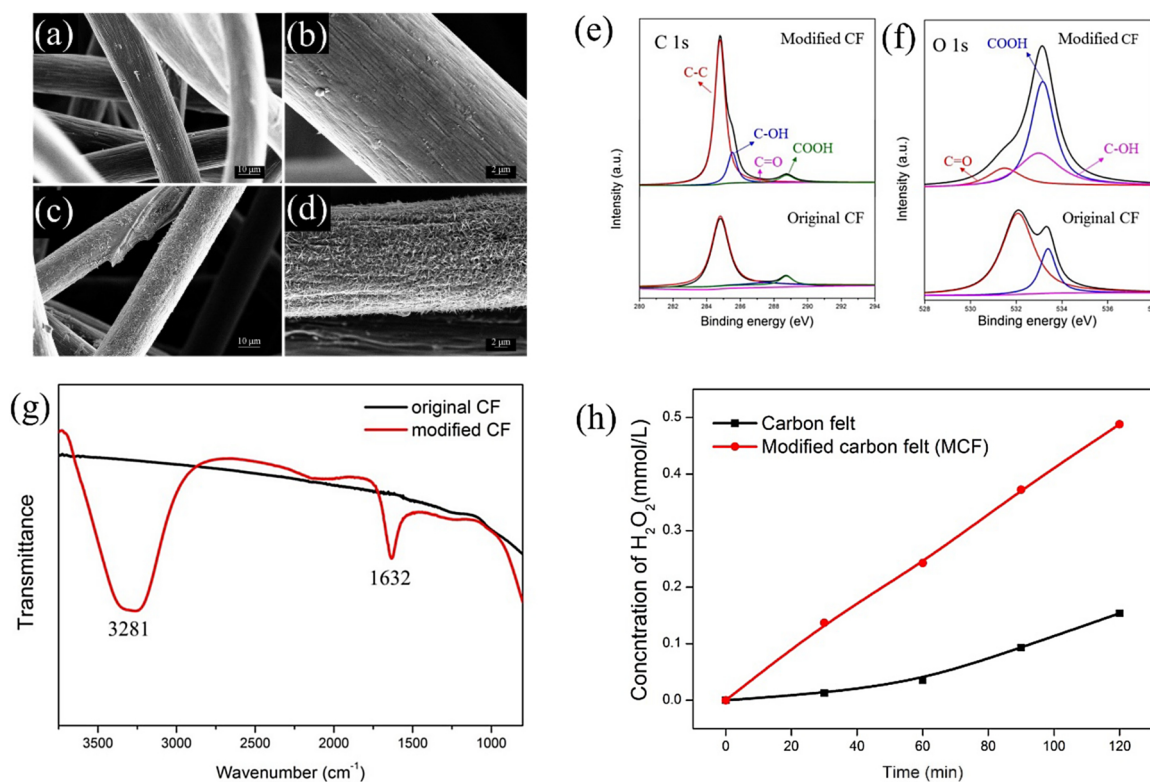
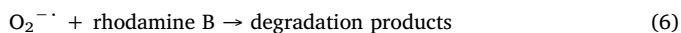


Fig. 3. (a), (b) SEM images of unmodified CF. (c), (d) SEM images of modified CF. XPS spectra of (e) C1s, (f) O1s peaks for the original and modified CFs. (g) FT-IR spectrum of original CF and modified CF. (h) Production of H₂O₂ for the original CF and modified CF.



In order to confirm the free radical produced in TNA-MCF/HCO₃⁻ systems, electron paramagnetic resonance (EPR) technique by using DMPO as trapping agent was carried out to determine the radical species in the system. EPR spectra was recorded by using an ESR/EPR spectrometer (Magnetech MiniScope, MS 5000). As shown in Fig. 4, $\cdot\text{CO}_3^-$ and $\cdot\text{OH}$ can be easily observed as previous articles reported [40,41]. Meanwhile, various uncertain peaks also arose in the spectrum. It was supposed that these peaks may be related to the singlet oxygen or superoxide radical which may be generated in the system, and the appearance of these radicals can decompose DMPO and thus produce uncertain peaks.

To further evaluate the validity of the above mechanism, free

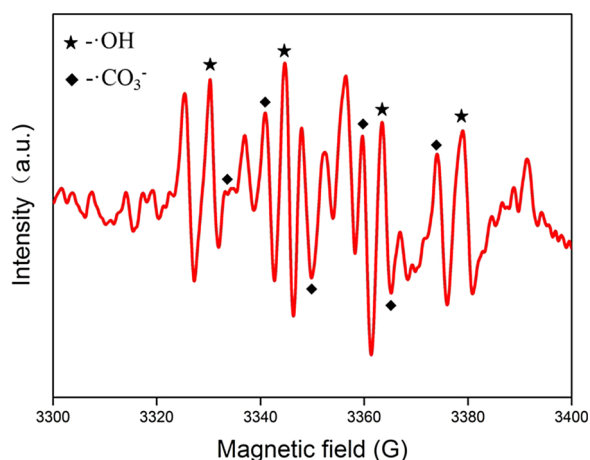


Fig. 4. DMPO spin-trapping EPR spectra in TNA-MCF/HCO₃⁻ system.

radical quantitative analysis and capture experiments were performed as Fig. 5 shown. Firstly, the amount of $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ radical were tested as previously reported [42] to confirm the function of different radicals in TNA-MCF/HCO₃⁻ system. As shown in Fig. 5a, the $\cdot\text{OH}$ amount after 120 min in these four PEC systems is all relatively low. Specially, the generation of $\cdot\text{OH}$ in HCO₃⁻ solution is much less than that of SO₄²⁻ system. It can be speculated that $\cdot\text{OH}$ may play little role in system based on HCO₃⁻ anion. The amount of $\text{O}_2^{\cdot-}$ generated in four PEC system is shown in Fig. 5b. It can be found that there is very few $\text{O}_2^{\cdot-}$ generation in TNA-Pt black/HCO₃⁻ and TNA-Pt black/SO₄²⁻ system. Notably, when the cathode changed to MCF, the concentration of $\text{O}_2^{\cdot-}$ got dramatically increased. The concentration of $\text{O}_2^{\cdot-}$ radical in TNA-MCF/HCO₃⁻ system is 0.38 mM, which is 47.5 times higher than that of $\cdot\text{OH}$ in the same system. Therefore, the function of $\cdot\text{OH}$ in TNA-MCF/HCO₃⁻ system is negligible. Besides, the $\text{O}_2^{\cdot-}$ radical amount in TNA-MCF/HCO₃⁻ system is also higher than that in TNA-MCF/SO₄²⁻ system. This is because that $\text{O}_2^{\cdot-}$ can be generated by both Eq. 3 and the reaction between H₂O₂ and HCO₃⁻ in TNA-MCF/HCO₃⁻ system [20,43]. Besides, according to the previous literatures, HCO₃⁻ can also activate H₂O₂ or $\text{O}_2^{\cdot-}$ to produce $\cdot\text{CO}_3^-$ radical [19–22]. The abundant $\text{O}_2^{\cdot-}$ radical generated from cathode may also contribute to $\cdot\text{CO}_3^-$ radical production.

Therefore, to verify the vital oxidant function of $\cdot\text{CO}_3^-$ radical, free radical capture experiments were performed. In quenching experiments, four different quenching agents, potassium iodide (KI), isopropanol (IPA), tert-butanol (t-BUOH) and benzoquinone were used respectively to determine the function of different radicals. Generally, IPA and t-BUOH were used for $\cdot\text{OH}$ radical capture because their fast reaction rate with $\cdot\text{OH}$ radical ($k_{\cdot\text{OH}/\text{IPA}} = 1.9 \times 10^9 \text{ m}^{-1}\text{s}^{-1}$, $k_{\cdot\text{OH}/\text{t-BUOH}} = 6 \times 10^8 \text{ m}^{-1}\text{s}^{-1}$) [44]. KI was often used for both hole and $\cdot\text{OH}$ capture [45]. Benzoquinone was served as $\text{O}_2^{\cdot-}$ scavenger. To minimize the influence of other factors like pH and illumination intensity, all experiments were performed in the same condition.

In TNA-Pt black/HCO₃⁻ system, the quenching results were shown

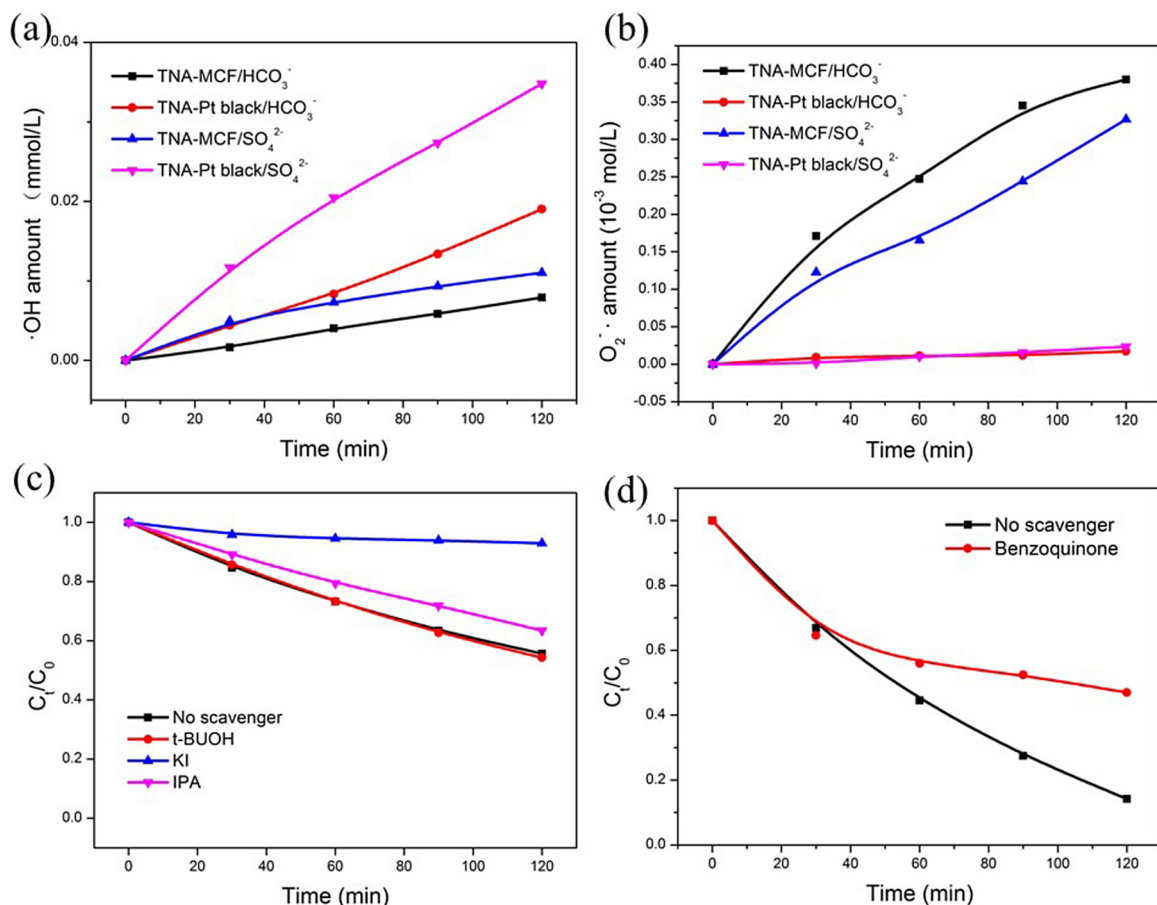


Fig. 5. (a) $\cdot\text{OH}$ amount measured in four PEC systems. (b) $\text{O}_2^{\cdot-}$ amount measured in four PEC systems. (c) Effects of radical scavengers on the degradation of RhB in TNA-Pt black/ HCO_3^- system. (d) Effect of radical scavenger on the degradation of RhB in TNA-MCF/ HCO_3^- system.

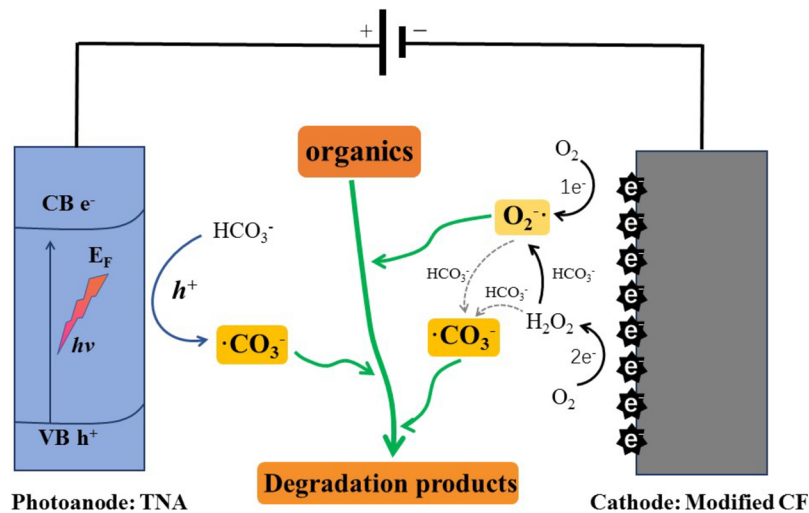


Fig. 6. Schematic illustration of efficiently degrading organics in TNA-MCF/ HCO_3^- system.

in Fig. 5c. it can be observed that KI almost prevented the process of degrade reaction. While as a comparison, the effects of IPA and t-BUOH were different. It can be found that t-BUOH almost hardly influence the degradation of RhB while IPA had certain prohibitive effect on pollutant degradation efficiency. Because the reaction constant between $\cdot\text{CO}_3^-$ radical and IPA ($k_{\text{CO}_3^-/\text{IPA}} = 4 \times 10^4 \text{ m}^{-1}\text{s}^{-1}$) is two orders of magnitude higher than that of t-BUOH. ($k_{\text{CO}_3^-/\text{t-BUOH}} = 1.6 \times 10^2 \text{ m}^{-1}\text{s}^{-1}$) [46]. Therefore, integrated with EPR result, it can be indicated that the predominant radical in TNA-Pt black/ HCO_3^- system is $\cdot\text{CO}_3^-$

which is mainly from the reaction between $h\nu^+$ and HCO_3^- (Eq.2). In addition, the ratio of $\cdot\text{CO}_3^-$ from different generation way is shown as following: about 30~37% RhB degraded by $\cdot\text{CO}_3^-$ produced by $h\nu^+$ (Eq.2) and 2%~9% RhB degraded by $\cdot\text{CO}_3^-$ produced by $\cdot\text{OH}$ ($\cdot\text{OH} + \text{HCO}_3^- \rightarrow \cdot\text{CO}_3^- + \text{H}_2\text{O}$).

Similarly, when using benzoquinone to capture $\text{O}_2^{\cdot-}$ in TNA-MCF/ HCO_3^- system, the degradation efficiency would be obviously hindered. As Fig. 5d shown, only 53% RhB can be degraded when adding benzoquinone as $\text{O}_2^{\cdot-}$ scavenger in TNA-MCF/ HCO_3^- system. This

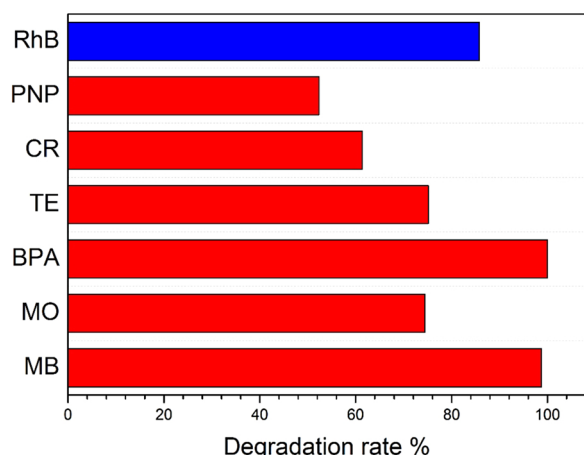


Fig. 7. Degradation of other organic pollutants. Conditions: NaHCO_3 0.05 M, methylene blue (MB) 20 mg/L, methyl orange (MO) 20 mg/L, congo red (CR) 20 mg/L, Rhodamine B (RhB) 20 mg/L, bisphenol A (BPA) 5 mg/L, P-nitrophenol (PNP) 5 mg/L, tetracycline (TE) 5 mg/L.

means that about 32% RhB is degraded due to $\text{O}_2^{\cdot-}$. Considering the role of Eq. (2) confirmed in TNA-Pt black/ HCO_3^- system, it can be inferred that the carbonate radical from the reaction between HCO_3^- anion with H_2O_2 or $\text{O}_2^{\cdot-}$ can responsible for 16%~23% RhB degradation [16,47]. To sum up, the degradation of pollutant in TNA-MCF/ HCO_3^- system is mainly based on the function of $\cdot\text{CO}_3^-$ and $\cdot\text{O}_2^-$ radical, but $\cdot\text{CO}_3^-$ still occupied primary position in degradation process.

3.4. The selectivity of TNA-MCF/ HCO_3^- system

In this paper, to further investigate the adaptation of TNA-MCF/ HCO_3^- system, versatile organic pollutants such as cationic dyes (MB), azo dyes (MO and CR), phenols (BPA and PNP) and antibiotics (TE) were chosen as model contaminants to examine the degradation efficiency under the same conditions. Fig. 7 shows the different organics degradation efficiency in TNA-MCF/ HCO_3^- system. RhB was displayed as a reference. Among these tested pollutants, MB and BPA could be completely degraded in 120 min; the removal ratio of MO, CR and TE was relatively lower, with 74.43%, 61.37% and 75.14% were removed respectively. While the degradation rate of PNP was the slowest, only 52.30% of PNP was removed after 120 min. As previous articles reported, $\cdot\text{CO}_3^-$ radical is a very selective electrophilic reagent which would tend to react with electron-rich moieties such as aromatic anilines, nitrogen containing compounds and sulfur containing compounds [48]. For instance, the reaction between phenol and $\cdot\text{CO}_3^-$ radical is over 10^3 faster than that of benzene ($k < 10^4 \text{ M}^{-1}\text{s}^{-1}$) [49]. Other reactants rate constants [50] were shown in Table S2. It can be seen that the highest rate constant is from the reaction between $\cdot\text{CO}_3^-$ radical and $\text{-N(CH}_3)_2$ ($k = 1.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$), followed by -NH_2 ($k = 5.4 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$) and -OH ($4.9 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$), which could explain the different efficiency displayed in Fig. 7. Therefore, these above results indicated that TNA-MCF/ HCO_3^- system was selective and would have a broad application in certain pollutants treatment.

4. Conclusion

Briefly, we described a novel PEC system of TNA-MCF based on carbonate radical for efficient organics degradation. In this system, HCO_3^- anion was used as electrolyte and free radical initiator. Both TNA photoanode and MCF cathode can strengthen $\cdot\text{CO}_3^-$ radical production and thus enhance the pollutants degradation. Results demonstrated that the TNA-MCF/ HCO_3^- system has an excellent performance in the degradation of refractory organics. Several influence factors like

pH value and HCO_3^- concentration were also investigated to reach optimal condition. In addition, the $\cdot\text{CO}_3^-$ based catalytic mechanism was proposed and also be successfully verified. Compared with traditional method, the PEC TNA-MCF/ HCO_3^- system has many advantages such as low expense, react rapidly and no extra pollution. Therefore, this system will have a broader application in organic wastewater treatment.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2019.118071>.

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